

Why Entropy?

■ Second Law of Thermodynamics:

The total entropy of an isolated system increases (or remains the same) in every thermodynamical process.

■ Macroscopic State variables:

- volume V ,
- temperature T ,
- mass m , mole number $n=N/N_A$, molecule number N ,
- pressure P ,
- internal energy U ,
- **entropy S .**

■ The following are **NOT** state variables, since they depend on the process (path), not on the state of the system:

- heat Q ,
- work W .

What is Entropy?

- An **infinitesimal** reversible process with heat exchange dQ_r causes an **entropy change**

$$dS = \frac{dQ_r}{T}.$$

- For a **finite** reversible process, the **entropy change** is

$$\Delta S = \int_i^f \frac{dQ_r}{T}.$$

- If the process is **irreversible**, we need to find an **equivalent reversible process** and calculate the integral for this reversible process.

Examples of Entropy Changes

- System **absorbs heat** => its entropy increases.
- System **expells heat** => its entropy decreases.
- In a reversible, **adiabatic** process, no heat is exchanged. Therefore, the entropy of the system does not change.

- Isothermal process:
$$\Delta S = \frac{Q_r}{T}$$

- Carnot cycle:
$$\Delta S = \frac{Q_h}{T_h} + 0 - \frac{Q_c}{T_c} - 0 = 0.$$

- Since the entropy S is a **state variable**, the entropy change is zero for **any closed path** over a reversible process.
$$\oint dS = \oint \frac{dQ_r}{T} = 0$$

- Example 15.4: **Melting** process:
$$\Delta S = mL_f / T_m.$$

More examples on Entropy changes:

- Example 15.7: Mixing process:

$$\Delta S = m_1 c_1 \ln(T_f/T_1) + m_2 c_2 \ln(T_f/T_2).$$

- Example 15.6: Free expansion:

$$\Delta S = nR \ln(V_f/V_i).$$

- Entropy on a microscopic scale
(statistical definition):

$$S = k_B \ln P.$$

where P is the probability of the state.